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Analysis of Combustion Chamber Deposits by ESI-TOF-MS and MALDI-TOF-MS

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Introduction. Combustion chamber deposits (CCDs) in internal combustion engines have been studied by various techniques to understand the relationship of performance degradation with deposit quantity and structure. XPS, XAS, NMR, and elemental analysis have offered insight into the bulk structure of C, H, N, O and metal components [1]. MS has offered some information about compound structure, but results are limited due to the insolubility and complexity of the materials. Recent advances in MS have opened new possibilities for analysis of CCDs. Here we report initial findings on the carbon structure of these deposits determined by ESI-TOF-MS and MADLI-TOF-MS.

Methods. The sample studied was taken from cylinder 1 block deposit of a 6-cylinder GM 3800 engine that was operated for 200 h on a standard fuel. The samples were soxhlet extracted with a 92 % CH_2Cl_2/ 8% CH_3OH (vol/vol) mixture. The solvent was removed from both fractions. The soluble fraction was further separated on a silica gel column using hexanes, CH_2Cl_2, 92 % CH_2Cl_2/ 8% CH_3OH, and DMF as elution solvents. The CH_2Cl_2 fraction was dissolved in a CH_2Cl_2/CH_3OH mobile phase and analyzed by ESI-TOF-MS in positive ion mode (flow rate 10 μL/min). The solvent was removed from the fraction and the solid was analyzed by MADLI-TOF-MS (no matrix was added). Infrared analysis was performed on the solvent-free fraction on a NaCl disk.

Results. The following discusses results only on the CH_2Cl_2 fraction from the silica gel separation of the soluble extract of the cylinder 1 block CCD. This sample shows IR bands indicating C=O (1712 cm^{-1}), C=C (1607 cm^{-1}), C–H (1300 cm^{-1}), and C–O (1207 cm^{-1}), typical of CCD [2]. Figure 1 shows the ESI-TOF-MS of the fraction at low and high cone voltages (30 and 180 V, respectively). The spectrum at the low cone voltage exhibits several homologous series separated by the repeating unit of m/z 72. Only singly charged ions are observed. The spectrum at the higher cone voltage exhibits a shift of these series to higher masses (extending past m/z 2000). In addition, in the low-mass range, new series are evident, also having the repeating unit of m/z 72. Figure 2 shows a expanded view of Figure 1. The individual series have the following relationships (m/z): B → A + 14.007, C → B + 14.007, D → C + 16.002, E → D + 14.007, X → Y + 28.032, W → X + 28.032. Exact mass differences show the repeating unit is 72.0575 Da, and this, combined with other spectroscopic evidence indicates a chemical composition of $C_4H_8O_1$. The differences in the m/z of the series A through Z are probably due to various end groups structurally related to the repeating unit. These structures are very similar to structures noted in the thermal degradation of poly(tetrahydrofuran) [3], suggesting a poly(ether) is a precursor and that the precursor went through the combustion chamber. Figure 3 shows the MALDI-TOF-MS of the fraction. The series seen in the ESI-TOF-MS data are evident at in the low-mass range. In addition more series are evident with repeating unit of 208 Da, extending far past m/z of 3000. These materials also have the behavior of a polymeric material, suggesting thermal degradation of a polymer precursor.

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[1] see, for example, Gasoline Performance and Additives, SAE SP-1396 (1998), ISBN 0-7680-0310-5, http://www.sae.org

[2] see, for example, Chemistry of Engine Combustion Deposits, L. W. Ebert, Ed. (1985), ISBN 0-306-41936-X Plenum Press, New York

[3] see, for example, R. P. Lattimer, J. Anal. Appl. Pyrolysis, 57, 57–76 (2001)

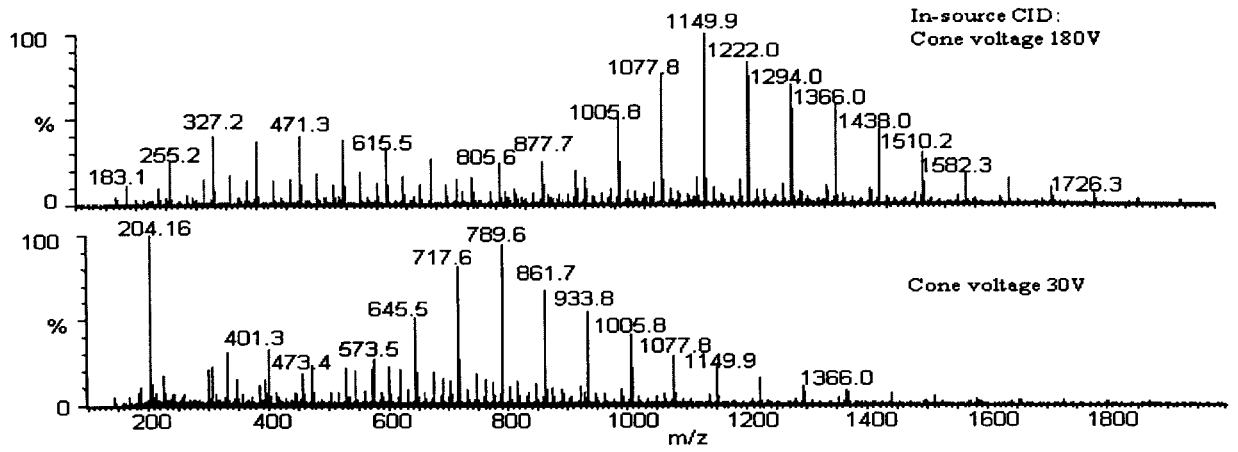

Figure 1.

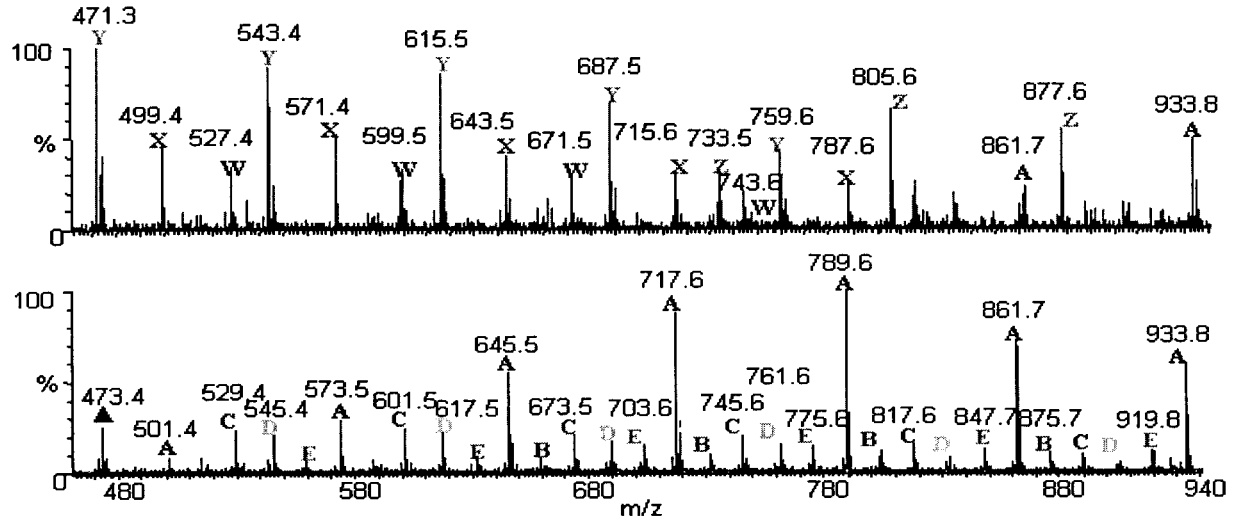

Figure 2.

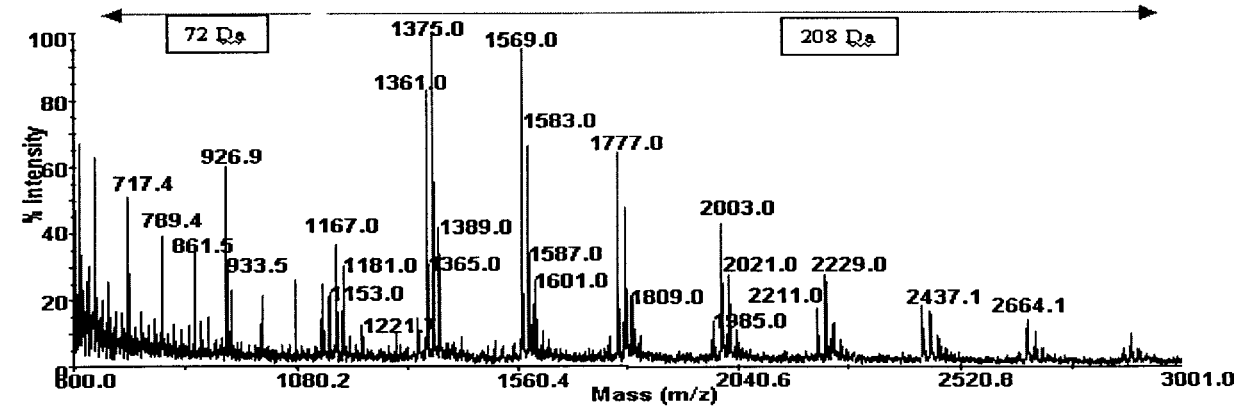

Figure 3.